

Nonequilibrium Glass Transition in Mixtures of Active-Passive Particles

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Abstract

We develop a mode coupling theory(MCT) to study the nonequilibrium glass transition behavior of a mono-disperse mixture of active-passive hard-sphere particles. The MCT equations clearly demonstrate that the glass transition is shifted to higher values of total volume fraction when doping a passive system with active particles. Interestingly, we find that the glass transition point may show a non-monotonic dependence on the effective diffusivity of the active component, indicating a nontrivial type of activity induced reentrance behavior. Analysis based on the nonergodic parameters suggest that the glassy state at small activity is due to the caging effect, while that at high activity could result from activity induced dynamic clustering.

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I. INTRODUCTION

The collective behavior of systems containing active particles have gained extensive attention in recent years due to its great importance both from a fundamental physics perspective and for understanding many biological systems[1, 2]. A wealth of new nonequilibrium phenomena have been reported, such as active swarming, large scale vortex formation[3, 4], phase separation[5–9], etc, both experimentally and theoretically. Recently, a new trend in this field has been the dynamics of dense assemblies of self-propelled particles around glass transition. Experiments on crowded systems of active colloids and active cells show dynamic features such as jamming and dynamic arrest that are very similar to those observed in glassy materials [10, 11]. Computer simulations demonstrated that nonequilibrium glass transition or dynamic arrest behavior does occur in a dense suspension of self-propelled hard spheres, where the critical density for glass transition shifts to larger value with increasing activity[12, 13] . Starting from a generalized Langevin equation with colored non-thermal noise, L.Brether and J. Curtin theoretically predicted that dynamic arrest can occur in systems that are far from equilibrium, showing that non-equilibrium glass transition moves to lower temperature with increasing activity and to higher temperature with increasing dissipation in spin glasses[14]. Mode coupling theory (MCT) were also proposed recently to study the glassy dynamics of driven granular fluids[15] and active colloidal suspensions[16].

While most of the studies so far have only considered single-component active particles, very recently, mixture systems of active-passive particles began to draw new attentions. Interesting experiments[5, 17] reported that the addition of active particles in a system can dramatically alter its phase behavior. Molecular dynamics simulation showed that introduction of activity to a passive system may not only hamper phase separation, but can enhance it as well, based on the coordination among the active particles [18]. It was also demonstrated that activity can induce phase separation and direct self-assembly in active-passive mixtures[9]. In particular, Brownian simulations showed that one may crystallize hard-sphere glass by doping with active particles[19], which proposes a very interesting question about the glass transition behavior of active-passive mixtures. However, an unified microscopic theoretical framework to describe this important issue is still lacking.

In the present paper, we develop a general MCT framework to study the glass transition behavior of active-passive mixtures. Our starting point is the Smoluchowski equation for N -

particle probability density function, wherein the particle activity is realized via an effective diffusivity that is larger than that of passive particles. Such a treatment allows one to apply the Mori-Zwanzig projection operator formalism such that a set of closed equations regarding the time evolutions of the density correlators can be obtained. In particular, we apply this approach to a binary mixture of mono-disperse active-passive hard sphere particles, with particular attention paid on how the particle activity and the number fraction of active particles would influence the glass transition behaviors. While doping with active particles can shift the transition to higher total volume fraction as expected, we find that increasing particle activity may lead to a nontrivial type of reentrance glass transition behavior.

II. THEORY

For generality, we consider an m -component mixture of N spherical colloidal particles, being active or not, dispersed in a simple fluid with temperature T and volume V . For passive particles, the over-damped dynamics can be described by Langevin equations involving the time evolution of the position vector \mathbf{r}_l^μ for an μ -type particle labeled l . For active particles, one generally needs to consider a further orientation variable ϑ_l^μ to account for the tumbling or rotational diffusion[20, 21]. Very recently, it was demonstrated that the dynamics of an active particle undergoing self-propulsion and rotational diffusion can be well-approximated by a random-walk in the long time limit with an effective diffusivity[20, 22]. These observations facilitate us to propose a minimal model for active-passive mixtures, which starts from the Smoluchowski equation for the probability density $P(\mathbf{r}^N, t)$ of the particle configuration $\mathbf{r}^N = \{\mathbf{r}_l^\mu\}_{l=1, \dots, N_\mu; \mu=1, \dots, m}$,

$$\partial P(\mathbf{r}^N, t) / \partial t = \hat{\Omega} P(\mathbf{r}^N, t) \quad (1)$$

where $\hat{\Omega}$ is the Smoluchowski operator

$$\hat{\Omega} = \sum_{\mu=1}^m \sum_{j=1}^{N_\mu} D_0^\mu \nabla_j^\mu \cdot (\lambda^\mu \nabla_j^\mu - \beta \mathbf{F}_j^\mu) \quad (2)$$

Here D_0^μ denotes the bare diffusivity for μ -type particles with total number N_μ and $\beta = 1/k_B T$ with k_B the Boltzmann constant. $\mathbf{F}_j^\mu = -\nabla_j^\mu U(\mathbf{r}^N)$ is the direct force acting on the particle $j \in \mu$ due to the total potential energy $U(\mathbf{r}^N)$ of the colloidal particles, and

∇_j^μ is the gradient operator with respect to \mathbf{r}_j^μ . A key factor here is the parameter λ^μ characterizing the particle activity of μ -species: $\lambda^\mu > 1$ for active particles while $\lambda^\mu = 1$ for passive ones. For an equilibrium distribution $P_e(\mathbf{r}^N, t) \propto e^{-\beta U}$, $\nabla_j^\mu P_e = +(\beta \mathbf{F}_j^\mu) P_e$ such that the random force balances the potential force for passive particles, but not for active ones.

To probe the collective dynamics of the system, one generally considers the density correlator

$$\Phi_{\mu\nu}(\mathbf{q}, t) = \left\langle \left(e^{\hat{\Omega}^\dagger t} \rho_{\mathbf{q}}^\mu \right) \rho_{-\mathbf{q}}^\nu \right\rangle \quad (3)$$

where $\rho_{\mathbf{q}}^\mu = \frac{1}{\sqrt{N_\mu}} \sum_{j=1}^{N_\mu} e^{-i\mathbf{q} \cdot \mathbf{r}_j^\mu}$ is the Fourier transform of the density $\rho^\mu(\mathbf{r}, t) = \frac{1}{\sqrt{N_\mu}} \sum_{j=1}^{N_\mu} \delta(\mathbf{r} - \mathbf{r}_j^\mu)$, and $\langle \cdot \rangle$ denotes an equilibrium average. $\hat{\Omega}^\dagger$ is the adjoint or backward Smoluchowski operator given by[16, 23, 24]

$$\hat{\Omega}^\dagger = \sum_{\mu=1}^m D_0^\mu \sum_{j=1}^{N_\mu} (\lambda^\mu \nabla_j^\mu + \beta \mathbf{F}_j^\mu) \nabla_j^\mu \quad (4)$$

where for arbitrary functions f and g of \mathbf{r}^N we have $\int d\mathbf{r}^N f(\hat{\Omega}g) = \int d\mathbf{r}^N (\hat{\Omega}^\dagger f) g$. The use of adjoint Smoluchowski operator facilitates us to apply Mori-Zwanzig approach and mode-coupling methods[24] to obtain an approximate dynamic equation for the density correlators (3) which reads in the matrix form as (See the Supplemental Information)

$$\begin{aligned} \frac{\partial}{\partial t} \Phi(q, t) + \mathbf{W}(q) \cdot \mathbf{S}^{-1}(q) \cdot \Phi(q, t) \\ + \int_0^t du \mathbf{M}(q, t-u) \cdot \mathbf{W}^{-1}(q) \cdot \frac{\partial}{\partial u} \Phi(q, u) = 0 \end{aligned} \quad (5)$$

Herein, $\mathbf{S}^{-1}(q)$ is the inverse of the partial structure factor matrix $\mathbf{S}(q) = \Phi(q, t=0)$, $\mathbf{W}(q)$ is a frequency matrix given by

$$W_{\mu\nu}(q) = q^2 D_0^\mu [(\lambda^\mu - 1) S_{\mu\nu}(q) + \delta_{\mu\nu}]. \quad (6)$$

$\mathbf{M}(q, t)$ denotes the matrix of so-called *irreducible* memory function[24–26] with elements given by

$$\begin{aligned} M_{\mu\nu}(q, t) = \frac{1}{2} \sum_{\mathbf{k}} \sum_{\delta\gamma\delta'\gamma'=1}^m V_{\mu;\delta\gamma}(\mathbf{q}, \mathbf{k}) V_{\nu;\delta'\gamma'}(\mathbf{q}, \mathbf{k}) \\ \times \Phi_{\delta\delta'}(k, t) \Phi_{\gamma\gamma'}(|\mathbf{q} - \mathbf{k}|, t) \end{aligned} \quad (7)$$

with vortex functions

$$V_{\mu;\delta\gamma}(\mathbf{q}, \mathbf{k}) = \frac{\rho D_0^\mu}{\sqrt{N_\mu}} [(\mathbf{q} \cdot \mathbf{k}) \delta_{\mu\gamma} C_{\mu\delta}(\mathbf{k}) + \mathbf{q} \cdot (\mathbf{q} - \mathbf{k}) \delta_{\mu\delta} C_{\mu\gamma}(|\mathbf{q} - \mathbf{k}|)] \quad (8)$$

where $\rho = N/V$ is the total number density and $C_{\mu\nu}(k) = \sqrt{x_\mu x_\nu} c_{\mu\nu}(k)$ in which $c_{\mu\nu}(k)$ are direct correlation functions. $C_{\mu\nu}(k)$ is related to the static structure factor via $\rho C_{\mu\nu} = \delta_{\mu\nu} - (\mathbf{S}^{-1})_{\mu\nu}$.

The MCT equations (5) to (8) for general active-passive mixtures constitute the first part of central results of the present paper. In general, one may employ them to study the glass transition or dynamic arrest behavior of any multi-component systems. In the present work, we will mainly focus on a two-component hard-sphere system, one is active labeled by 'a' and the other is passive labeled by 'p'. For simplicity, we consider that the diameters d of both types of particles are the same. The total volume fraction is given by $\varphi = \rho\pi d^3/6$, with d set to be 1. The number fraction and the activity parameter of the active component are given by x_a and λ_a respectively, which are chosen as the main control parameters in the present study. Eqs.(5) are numerically solved with Percus-Yevick static structure factors $S_{\mu\nu}(k)$ ($\mu, \nu = a$ or p) as input and setting $D_0^a = D_0^p = 1$. For a pure passive system with $x_a = 0$, the equations predict a glass transition (GT) at volume fraction $\varphi_c^0 = 0.515$.

III. RESULTS AND DISCUSSION

First of all, we study how the particle activity influences the GT. To this end, we fix $x_a = 0.5$ and set $\varphi = 0.524$ which is above the GT point φ_c^0 for pure passive system. In Fig.1(a), we show the time evolution of the dynamic scattering functions $\Phi_{aa}(k, t)$ and $\Phi_{pp}(k, t)$ evaluated at $k = k_m$, where $k_m \simeq 7.23$ is the location of the first peak in S_k , with varying particle activity λ^a in a relatively small range. When λ^a is just slightly than one, e.g., $\lambda^a = 1.02$, both correlators do not decay in the long time and the system remain in the glassy state. The nonegodicity parameter $f_k^a = \Phi_{aa}(k, t \rightarrow \infty)$ for the active particle (dashed line) is slightly slower than $f_k^p = \Phi_{pp}(k, t \rightarrow \infty)$ for the passive particle, indicating that the glassy part formed by the active component is softer than the passive part. With increasing λ^a , the plateau heights of both correlators decrease. Above some threshold value

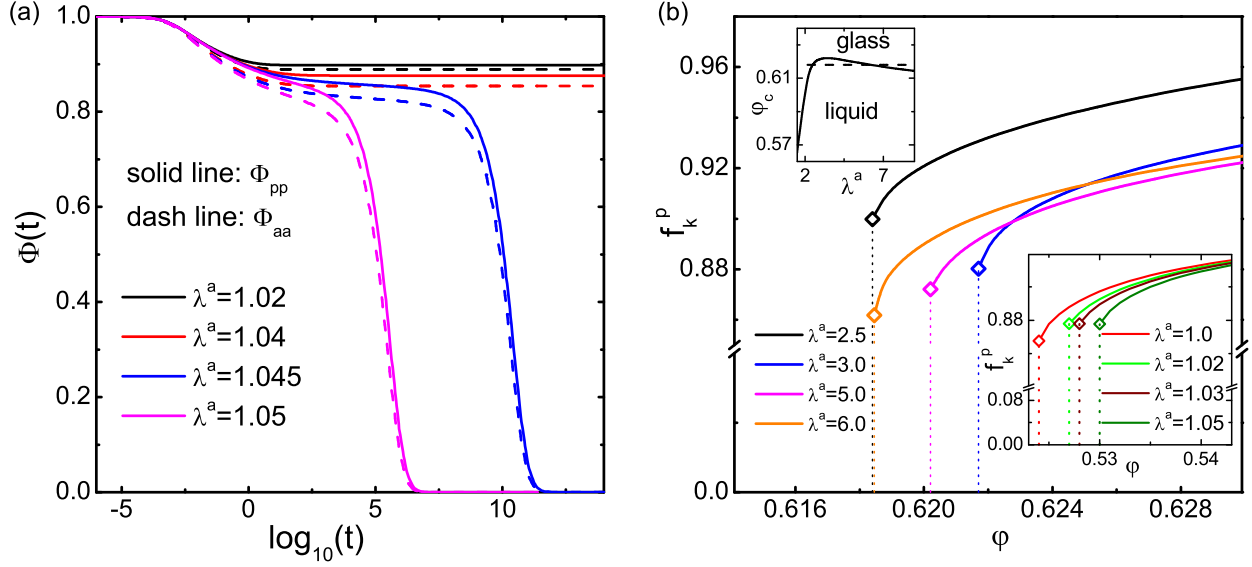


Figure 1: (Color online) (a) Dynamic scattering functions $\Phi_{pp}(k, t)$ for passive particles (solid lines) and $\Phi_{aa}(k, t)$ for active particles (dashed lines) evaluated at $k = k_m$ for different values of the activity parameter λ^a . The total volume fraction is $\phi = 0.524$ and the number fraction of active particles is $x_a = 0.5$. (b) Dependences of the non-ergodic parameters f_k^p evaluated at $k = k_m$ on the total volume fraction ϕ for different values of λ^a and $x_a = 0.5$. The right inset shows f_k^p for several values of λ^a close to 1.0 for clarity. The left inset plots the dependence of ϕ_c on λ^a where a turnover phenomenon is apparent, wherein the dashed line refers to $\phi = 0.618$ where the system shows reentrance behavior. See the text.

of λ^a (about 1.044 here), the correlators finally decay to zero and the system becomes fluid, wherein the active component relaxes faster than the passive one.

Above results clearly demonstrate that increasing activity of the active component can shift GT to higher volume fractions. In Fig.1(b), we plot the nonergodic parameters f_k^p evaluated at $k = k_m$ as functions of the total fraction ϕ for several different values of λ^a . As it should, f_k^p takes a finite value at a certain discontinuous glass transition point ϕ_c before which $f_k^p = 0$. Clearly, the value of ϕ_c increases fast with λ^a at first, e.g., $\phi_c \simeq 0.515$ for $\lambda^a = 1.0$ and $\phi_c \simeq 0.622$ for $\lambda^a = 3.0$. Strikingly, however, with further increasing of λ^a to larger values like 5.0, ϕ_c decreases again to a smaller value around 0.620. In the left inset of Fig.1(b), the dependence of ϕ_c on λ^a is shown, where the turnover phenomenon is apparent.

The above findings indicate an interesting type of reentrance behavior in active-passive mixtures for a fixed total volume fraction ϕ . For instance, for $\phi = 0.618$ as indicated by

the dashed line in the left inset of Fig.1(b), the system changes first from glass to liquid and then to glass again as λ^a increases. While the first transition from glass to liquid is as expected because activity can push the glass transition to higher volume fraction, the second one from liquid to glass again is rather counterintuitive. To get more insight, we have plot the nonergodic parameters f_k^a and f_k^p for all wave vectors in Fig.2(a) for $\varphi = 0.618$ and λ^a from 1.05 to 6.0. For $\lambda^a = 1.05$ where the system is in glassy state, we see that the profiles of f_k^a and f_k^p are nearly the same, with only slight differences in their values. For $\lambda^a = 2.0$, the system is still glass, with the active part much softer than the passive part. For $\lambda^a = 3.0$ and 4.0, the system is in the liquid phase because all the f_k s are now zero. Nevertheless, for further larger values of λ^a , say 5.0 and 6.0, the system becomes glassy again since both f_k^a and f_k^p have nonzero values in some k range. Interestingly, we find that the profiles of f_k^a and f_k^p are quite different in this latter case. f_k^p remains a relatively large value and contains many peaks indicating the passive component is frozen at all length scales but with a certain type of structure. However, f_p^a is only apparently nonzero for small k and is almost zero for k larger than some threshold value, suggesting that the active part is still liquid-like in short length scales but being frozen in large scales.

We note here that a few interesting reentrance behaviors regarding glass transition have been reported in the literatures. For instance, for passive hard-spheres with short-range attractions, it was found that increasing the attraction can melt glass, however, further increasing attraction can lead to glass again[27]. The reentrance was due to the existence of two qualitatively different glassy states: one with structural arrest due to caging and the other with arrest due to bonding. For passive hard sphere mixtures with very disparate sizes, reentrance behavior[28] as well as multiple glasses[29] have also been reported. Reentrance glass transition has also been found for fluids in porous media, where for large volume fraction of immobile matrix particles, increasing or decreasing the number fraction of fluid particles may both lead to glassy states[30, 31]. Multiple reentrant glass transitions were also found in a confined system of hard spheres between two parallel walls[32]. Here we report a new type of reentrance glass transition behavior induced by particle activity. As demonstrated in Fig.2, the reentrance here may be also due to existence of two types of nonequilibrium glassy states. For small activity, the dynamic arrest is due to the caging effect of both passive and active particles. Increasing activity acts as 'noise' which can destroy the cages and melt the glass. If activity is too large, however, local phase separation[5–9] of the active

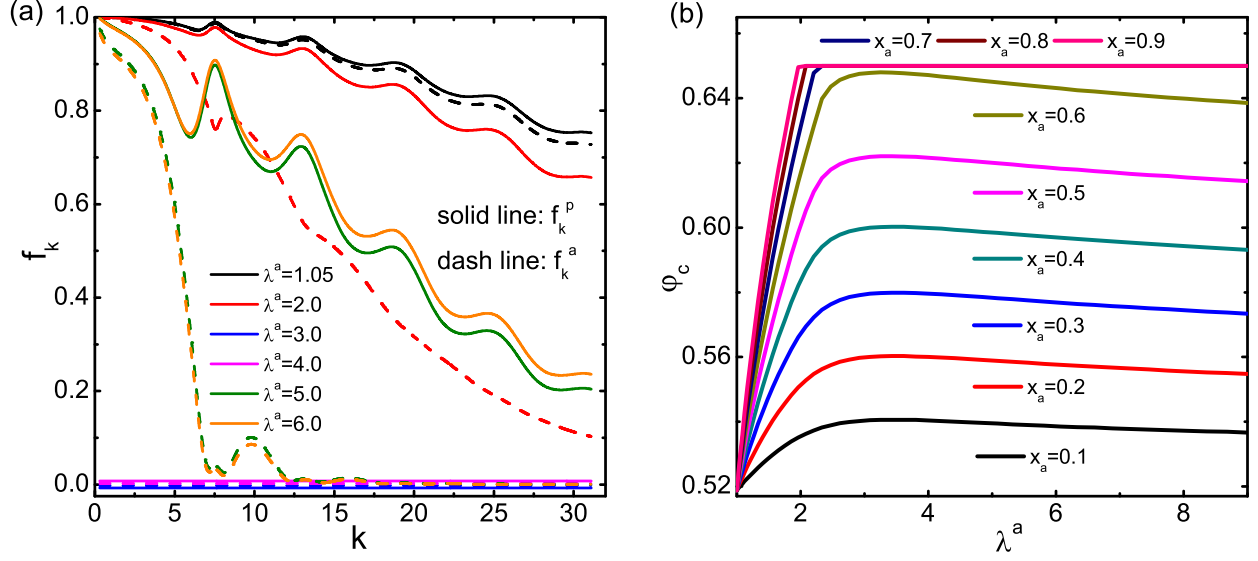


Figure 2: (Color Online) (a) Non-ergodic parameters f_k^p (solid lines) and f_k^a (dashed lines) in the whole k range for different values of λ^a at fixed total volume fraction $\varphi = 0.618$ and $x_a = 0.5$ where reentrance behavior can be observed. For relatively large $\lambda^a = 5.0$ and 6.0, f_k^a is nearly zero for large k and apparently nonzero for small k . (b) Dependence of the glass transition point φ_c on particle activity λ^a for different x_a . Reentrance behavior disappears if x_a is too large.

particles could happen such that active particles can form local clusters, which may also leads to dynamic arrest. In this case, the non-clustered active particles can still move like liquids within small length scales, such that f_k^a is nearly zero for large k . It is interesting to check such a scenario by large scale computer simulations, which definitely deserves a separate future work. We would like to mention here that in a recent simulation work of active-passive mixtures[9], the authors demonstrated that the active component triggers phase separation into a dense and a dilute phase, where active-passive segregation were further observed in the dense phase with rafts of passive particles in a sea of active particles. We suggest that the reentrant glassy state for large activity we found in the present work may look like this type of active-passive segregation in dense phase.

We now consider how the above results depend on the number fraction x_a of the active component. In Fig.2(b), the dependences of φ_c on λ^a for different values of x_a are shown. Clearly, the reentrance behavior can occur in a large range of values of x_a . But for too large x_a , φ_c will become saturated to a value about 0.65, which is consistent with the result for a pure active system[16]. Thus one conclude that the interesting reentrance behavior

reported above is a specific feature of active-passive mixture system and cannot occur for a pure active system. The data also indicates that φ_c increases monotonically with x_a for a fixed λ^a , which is in consistent with the simulation work of R. Ni *et al.* that doping active particles can help crystallizing hard spheres by melting glass[19]. Note that the reentrance behavior does not exist with variation of x_a .

IV. CONCLUSION

In conclusion, we have developed a mode-coupling theory starting from Smoluchowski equations to study the nonequilibrium glassy dynamics in mixtures of active-passive particles. This microscopic theory makes it convenient to study the relaxation of the density correlators and make predictions about the liquid-glass transition boundaries. In particular, we have applied our theory to investigate the glass dynamics of a binary mixture of mono-disperse active-passive hard spheres. The theory clearly demonstrates that doping with active particles will push the critical volume fraction φ_c for glass transition to higher values. In addition, we find an interesting type of reentrance behavior induced by particle activity. For a certain given total volume fraction where the system is in glassy state without activity, increasing the activity level will first melt the glass, while further increasing activity may lead to a glassy state again. The k -dependent nonergodic parameters for the active and passive components share similar profiles in the former glass state, while they are quite different in the latter one, wherein the active particles are frozen in large scales but remain fluid-like in small ones. Such a reentrance behavior is found to be a specific feature of a mixture system, while it is absent in a pure active system. We believe that our present work can offer more perspectives in the study of collective dynamics of active-passive mixtures, as well as the frontier topic regarding nonequilibrium glass transition.

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